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## The structure of amorphous Si–Ni alloys

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EXAFS data has been obtained from both absorption edges for a series of amorphous Si–Ni alloys prepared by RF sputtering in thin film form over the whole composition range.

All samples show a degree of chemical order, which apparently increases with increasing nickel content, with largely invariant interatomic distances and Debye-Waller factors. Small Angle X-ray Scattering shows that the samples containing less than 50% nickel are phase-segregated on the 30Å scale.

The experimental data for the low-nickel samples is interpreted in terms of an amorphous NiSi phase distributed within an amorphous Si matrix. High-nickel samples are single phase, showing a high degree of chemical order.

**Keywords:** amorphous solids, structure, phase segregation

### 1. Introduction.

Transition metal silicides have been studied in depth both because of their potential device applications and to increase the understanding of the metal-insulator transition (MIT). Amorphous samples are particularly convenient for MIT studies since their composition can be varied smoothly across a wide composition range. Studies of amorphous  $\text{Si}_{1-x}\text{Ni}_x$  generally show a MIT at between 10 and 20 atomic per cent nickel (Colver, 1977, Dammer, et al, 1993) and our optical data (Williams, 1996) are in agreement with this, showing the band gap going to zero at about 15% nickel content. The interpretation of the MIT depends on whether the samples are structurally homogeneous or phase-segregated on a microscopic scale.

We present here an EXAFS study of the local structure of  $\text{Si}_{1-x}\text{Ni}_x$  amorphous thin films with  $x$  varying from 0.0 to 0.74, together with the results of a Small Angle X-ray Scattering (SAXS) study designed to detect phase segregation on a scale of tens of Angstrom.

### 2. Experimental Method.

EXAFS data were obtained on stations 7.1 (Ni K edge) and 3.4 (Si K edge) of the Daresbury SRS. Beam currents during data taking were about 200mA. Station 7.1 has a silicon (111) monochromator: harmonic rejection was achieved using a 50% detune. Standard transmission geometry was used. Station 3.4 has a pre-mirror to reject harmonics and has an InSb (111) monochromator. Total electron yield was used to measure the X-ray absorption. SAXS data was collected on station 8.2 using a camera length of 1.5m, X-rays of wavelength 1.5Å and a 512 channel proportional counter.

The EXAFS data were calibrated and background-subtracted using standard Daresbury software and analyzed using the Daresbury program EXCURV92. Single-scattering fast curved wave theory (Gurman, et al, 1984) was used throughout, with scattering parameters calculated within the program from a complex, energy-dependent Hedin-Lundqvist potential.

The Ni K edge data (Figure 1) were of high quality with a usable  $k$  range of  $2-15\text{Å}^{-1}$  for all samples, enabling two shells to be reliably fitted. The Si K edge data were poorer, the usable  $k$  range being only  $2-11\text{Å}^{-1}$ . Again, two shells contributed significantly to the fits.

### 3. EXAFS and SAXS Results.

The results of the EXAFS analysis are shown in Table 1, which gives the fitted values of the bond lengths  $R_{ij}$ , the partial coordinations  $N_{ij}$  and the mean square variations in distance  $\sigma_{ij}^2$ . The structural parameters for the Ni–Si coordination obtained from analysis of the Ni and Si edge data are always consistent ( $R_{\text{NiSi}}=R_{\text{SiNi}}$ ,  $\sigma_{\text{NiSi}}^2=\sigma_{\text{SiNi}}^2$ ,  $xN_{\text{NiSi}}=(1-x)N_{\text{SiNi}}$  within their uncertainties. These results are also consistent with those previously reported (Edwards, et al 1989; Asal, et al 1992).

We note that the Ni environment is invariant (in  $R$ ,  $N$  and  $\sigma^2$ ) for  $x<0.5$ . This is apparent in the EXAFS on the nickel K edge, shown as Figure 1, which is very similar for all samples. At higher nickel contents, the coordination numbers vary. The Si–Si distance rises from 2.34Å to 2.44Å in the same composition range and is constant thereafter. For the Si–Si coordination  $\sigma^2$  is constant for  $x>0.5$ . These results are considered further below.

Our SAXS results (Williams 1996) show a Guinier peak at low  $k$  in all samples. The amplitude of this peak is independent of composition and we interpret it as due to voids introduced during deposition (Williams, et al 1995). Samples in the composition range  $0.12<x<0.48$  also show a second peak at higher  $k$ . The amplitude of this peak is a maximum around 20–30 at % Ni and it is absent from all samples with  $x>0.5$ . The presence of this peak indicates the presence of two phases in the samples with  $x<0.5$ , and the variation in its amplitude implies segregation into amorphous Si and amorphous NiSi regions. Its position indicates a scale of 30–40Å for the phase segregation.

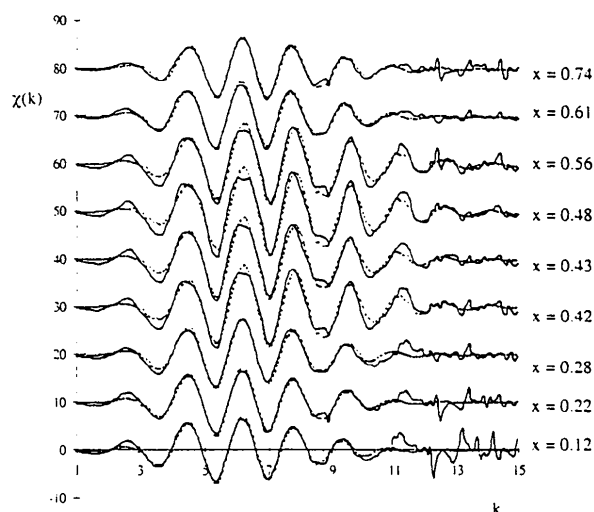


Fig. 1. EXAFS spectra on the nickel K edge from amorphous  $\text{Si}_{1-x}\text{Ni}_x$ . Note the strong similarity between these spectra.

#### 4. Discussion.

The EXAFS and SAXS results shown may be interpreted consistently in terms of a simple model of the structure of these amorphous  $\text{Si}_{1-x}\text{Ni}_x$  thin films. We suggest that the samples are phase-segregated, on the 20-30Å scale, into regions of amorphous Si and amorphous NiSi when  $x < 0.5$ . For  $x > 0.5$  they comprise a single amorphous phase. Such a model comes directly from the SAXS results.

For  $x > 0.5$ ,  $R_{ij}$  and  $\sigma^2_{ij}$  are constant for all bonds. Both Ni and Si are reasonably close-packed and the coordination numbers suggest that chemical order is almost complete. The interatomic distances are similar to those seen in crystalline nickel silicides. We suggest that our samples are behaving as typical (metallic) amorphous metal-metalloid compounds in this composition range.

For  $x < 0.5$ , we suggest that our samples are phase segregated into an amorphous Si and an amorphous NiSi phase, segregation occurring on the 20-30Å scale. The nickel environment found for  $x < 0.5$  is then that of the NiSi phase, so that  $R_{ij}$ ,  $N_{ij}$  and  $\sigma^2_{ij}$  are all independent of composition. The silicon environment is a mixture of amorphous Si ( $R = 2.34\text{Å}$ ,  $N = 4$ ,  $\sigma^2 = 60 \cdot 10^{-4} \text{Å}^2$ ) and the amorphous NiSi which has  $R_{\text{SiSi}} = 2.44\text{Å}$ ,  $N_{\text{SiSi}} = 2$ ,  $R_{\text{SiNi}} = 2.32\text{Å}$ ,  $N_{\text{SiNi}} \sim 7$  (and  $R_{\text{NiNi}} = 2.53\text{Å}$ ,  $N_{\text{NiNi}} = 2$ ). These distances and coordinations are similar, but not identical, to those found in crystalline NiSi. The mean square variation in distances suggest a fair amount of non-thermal disorder, except for the Si-Si coordination (which also shows no such disorder in amorphous silicon).

The predictions of this model are shown as the dashed and solid lines on Figure 2: the invariant Ni environment which it predicts is apparent from the data presented in Table 1. We note that the model gives reasonably good predictions of the composition variation of the Si-Si distance and of the Si-Si and Si-Ni coordinations. The presence of two different Si-Si distances (2.34Å and 2.44Å) in the two phases will also lead to a roughly parabolic variation in the mean square variation of Si-Si. Such a variation is apparent in Table 1, although the model will only account for a maximum variation in  $\sigma^2_{\text{SiSi}}$  of about  $40 \cdot 10^{-4} \text{Å}^2$ , rather less than that found.

#### 5. Conclusions.

Our EXAFS and SAXS results have enabled us to obtain a fairly detailed picture of the structure of amorphous thin films of  $\text{Si}_{1-x}\text{Ni}_x$ , prepared over the whole composition range. Our main conclusion is that these materials are phase-segregated, on the 20-30Å scale, into amorphous Si and amorphous NiSi so long as  $x < 0.5$ . Samples with higher nickel contents are single-phase, with structures similar to many other amorphous metal-metalloid alloys.

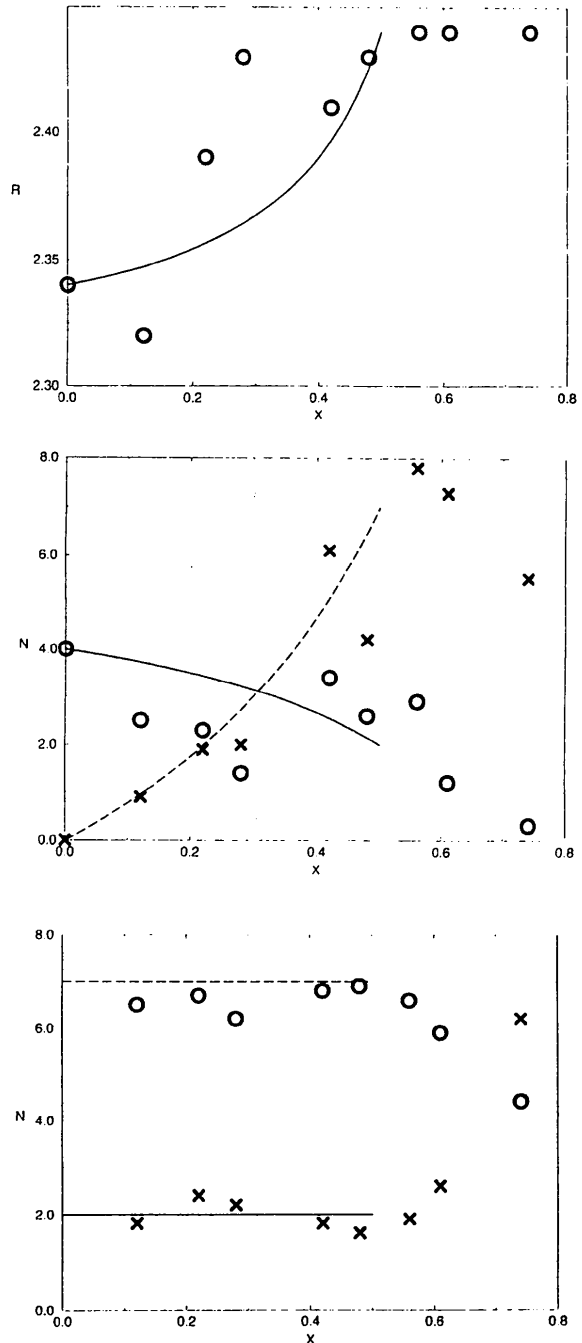


Fig 2. Fitted parameters and model predictions.  
 a) Si-Si (O) distances and model predictions (solid line).  
 b) Si-Si (O) and Si-Ni (X) coordinations. Solid lines: predictions for Si-Si; dashed line: prediction for Si-Ni.  
 c) Ni-Ni (X) and Ni-Si (O) coordinations. Solid line: prediction for Ni-Ni; dashed line: prediction for Ni-Si

Table 1: EXAFS results for amorphous  $\text{Si}_{1-x}\text{Ni}_x$  thin films

x	R A (SiSi)	R A (SiNi)	R A (NiSi)	R A (NiNi)	N (SiSi)	N (SiNi)	N (NiSi)	N (NiNi)	$\sigma^2 A^2$ (SiSi)	$\sigma^2 A^2$ (SiNi)	$\sigma^2 A^2$ (NiSi)	$\sigma^2 A^2$ (NiNi)
0.00	2.34	-	-	-	4.0	-	-	-	60	-	-	-
0.12	2.32	2.35	2.33	2.53	2.5	0.9	6.5	1.8	60	110	120	150
0.22	2.39	2.30	2.34	2.53	2.3	1.9	6.7	2.4	120	110	120	160
0.28	2.43	2.32	2.34	2.55	1.4	2.0	6.3	2.2	140	200	140	150
0.42	2.41	2.32	2.34	2.52	3.4	6.1	6.8	1.8	40	100	80	200
0.43	2.44	2.34	2.34	2.49	3.6	8.6	6.6	1.3	40	120	60	130
0.48	2.43	2.33	2.34	2.47	2.6	4.2	6.9	1.4	50	100	60	140
0.56	2.44	2.33	2.33	2.49	2.9	9.8	6.5	1.9	40	140	80	160
0.61	2.44	2.33	2.35	2.55	1.2	7.3	5.9	2.7	60	160	100	130
0.74	2.44	2.35	2.37	2.56	0.3	5.5	4.8	6.2	50	140	100	180
	$\pm 0.02$	$\pm 0.02$	$\pm 0.02$	$\pm 0.02$	$\pm 0.5$	$\pm 1.0$	$\pm 0.5$	$\pm 0.5$	$\pm 30$	$\pm 30$	$\pm 30$	$\pm 30$

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